Project ID: bat319

Advanced Microscopy and Spectroscopy for Probing and Optimizing Electrode-Electrolyte Interphases in High-Energy Lithium Batteries

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Overview

Timeline

- October 1st, 2016
  (delayed start Feb. 2017)
- September 30th, 2019
  (NCE to Jan. 2020)
- Percent complete: 35%

Barriers

- Barriers addressed
  - Anion redox and oxygen evolution
  - Poor voltage stability
  - Interface chemical changes and structure instability

Budget

- Total project funding
  - US$ 1,200,000 (10% non-federal matching)
- Funding received in FY17
  - US$ 424,800
- Funding for FY18
  - US$ 424,800 (matching non-federal US$47,200)

Partners

- Interactions/ collaborations
  - Oak Ridge National Lab
  - Cornell University
  - Argonne National Lab
  - Ningbo Institute of Materials Technology and Engineering China
  - Battery500 Consortium

Relevance and Project Objectives

- Combine atomic resolution scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), operando Bragg Coherent Diffraction Imaging (BCDI), and first principles computation to probe anion redox and oxygen evolutions in Li-excess NMC materials.

- Track the lithium and oxygen dynamics under electrochemical testing via operando neutron diffraction which will enhance the understanding of the overall structural changes due to anion activities.

- Investigate synthesis approach to produce the modified materials with the optimum bulk compositions and surface characteristics at large scale for consistently good performance.

- The above mentioned characterization tools will be extended to diagnose various anode types, such as Li metal anode.

Approaches/Milestones

- Structure recovery demonstration of Li-rich layered oxide after cycling (Sept.-17). - **Complete**

- Neutron diffraction characterization and microstrain analysis of Li-rich layered oxide for structure recovery (Sept.-17). **- Complete**

- Investigation of nanoscale LLTO (Lithium Lanthanum Titanium Oxide) surface coating effect on Li-rich layered oxide (Dec.-17). **- Complete**

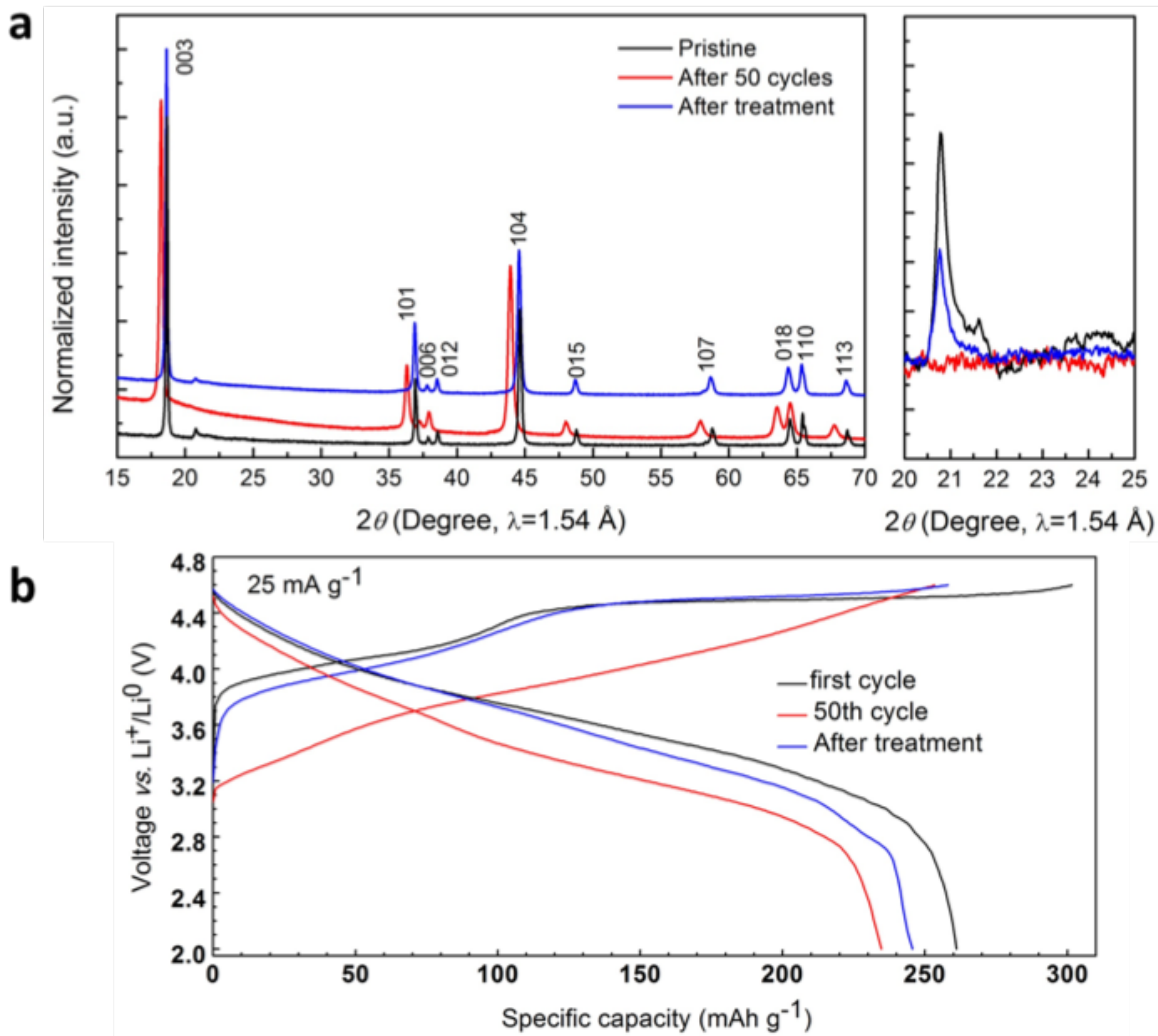
- Chemical composition and structure of electrochemically deposited Li metal at nano scale (Dec.-17). **– Complete**

- BCDI characterization on single particle of Li-rich layered oxide during electrochemical cycling (June-18). **– On track**

- Influence of metal-ion electrolyte additive on electrochemically deposited Li metal (June-18). **– On track**

Accomplishment to Date FY 18

Structure Recovery Demonstration of LRLO after Cycling

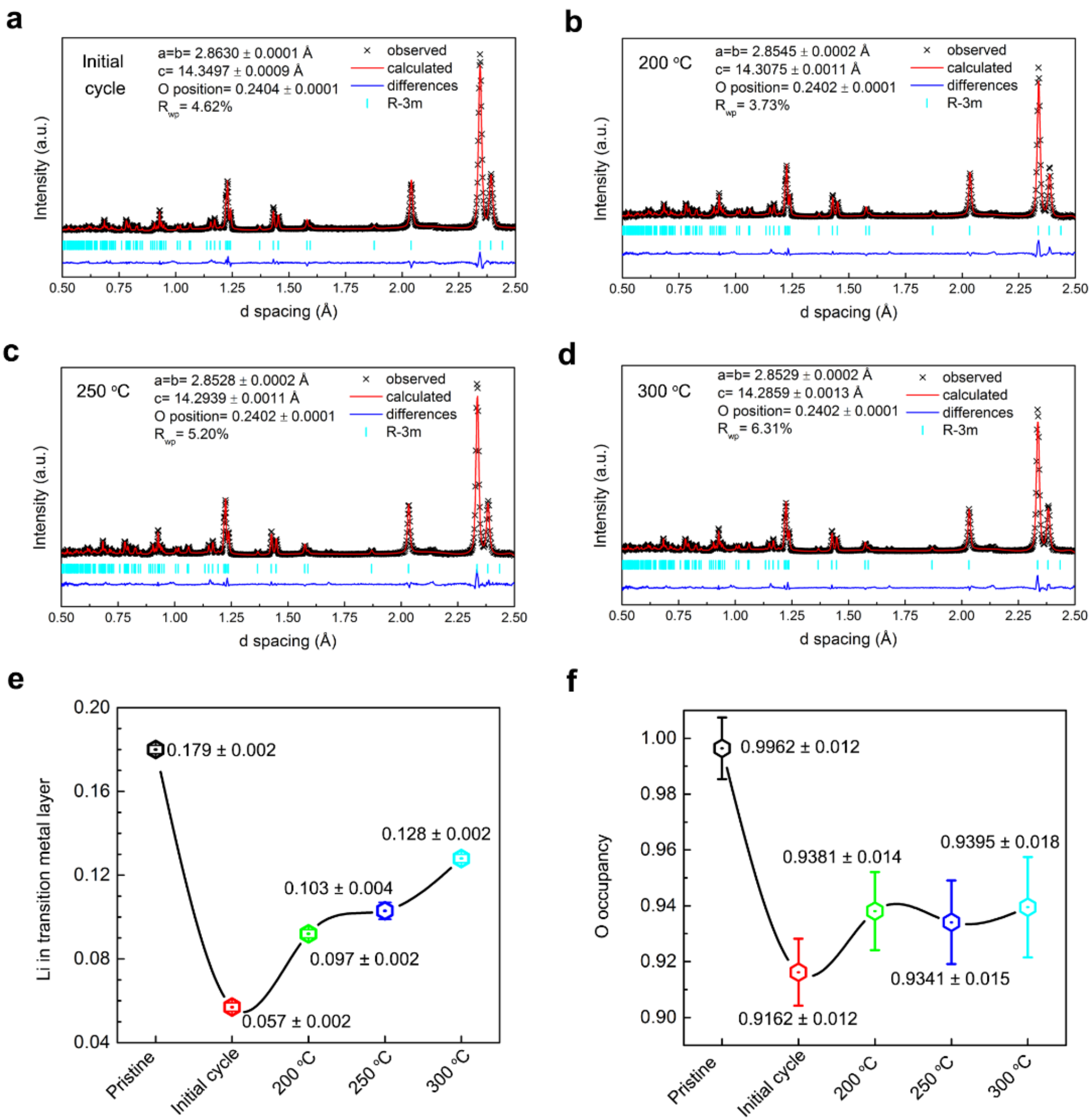


- ❑ The superstructure peak between 20° and 25° disappears after 50 cycles, which indicates the material becomes partially disordered.
- ❑ After heat treatment, the superstructure peak is recovered, which indicates the bulk structure is reordered.
- ❑ The superstructure recovery is decisive in restoring the original voltage output of LRLO cathode.

M. Zhang, B. Qiu, Y.S. Meng et al., 2018, under review

Accomplishment to Date FY 18

Neutron Diffraction Characterization of LRLO after Recovery



- ❑ Both *a* and *c* lattice parameters are reduced after annealing under different temperature, which indicates structure transformation occurs with strain decrease.
- ❑ Lithium from the TM layer is largely irreversible with only 32% of lithium reinsertion. Oxygen vacancies are also observed in the cycled sample.
- ❑ It is found Li occupancy in the TM layer and oxygen occupancy increase for the cycled sample after heat treatment.

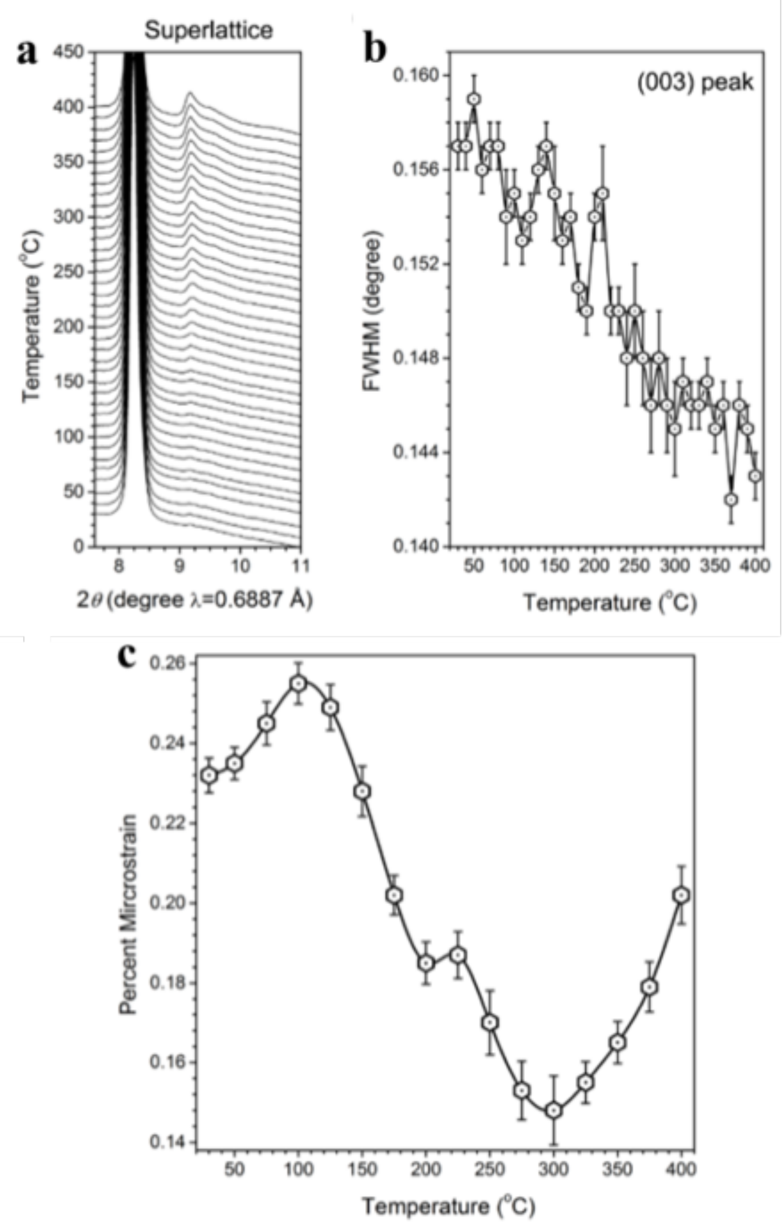
M. Zhang, B. Qiu, Y.S. Meng et al., 2018, under review

Accomplishment to Date FY 18

Microstrain Analysis of LRLO after Structure Recovery

- ❑ Operando SXRD was also performed for the samples after 50 cycles in the same temperature range and the same phenomenon is confirmed based on the reappearance of the superlattice peak.

- ❑ After the heating temperature is higher than 150°C, the microstrain suddenly decreases and reaches to its minimum value at a temperature around 300°C. The strain release is originated from the defects elimination.

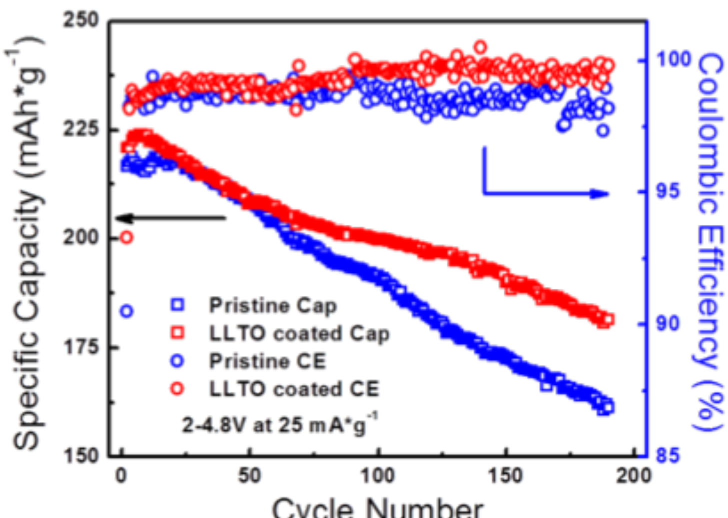


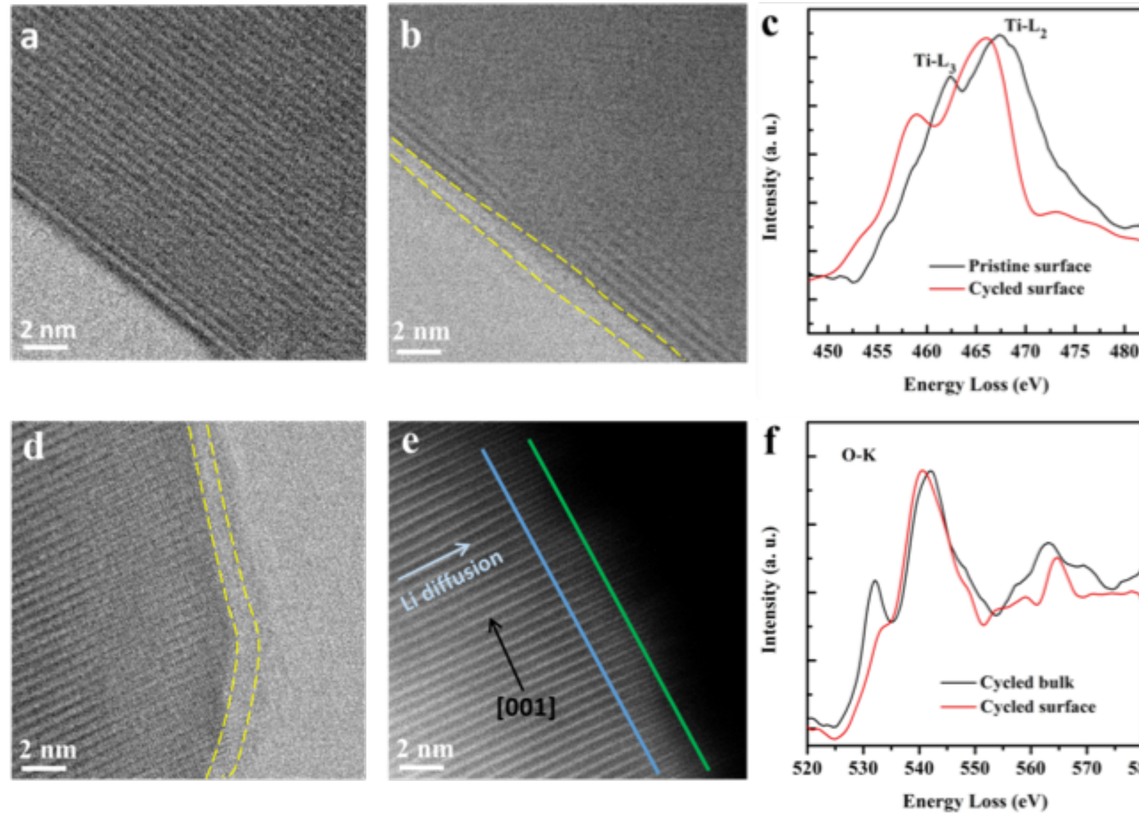
M. Zhang, B. Qiu, Y.S. Meng et al., 2018, under review

Accomplishment to Date FY 18

Investigation of LLTO Surface Coating Effect on LRLO

- ❑ LLTO coating could significantly improve cycling columbic efficiency and capacity retention.





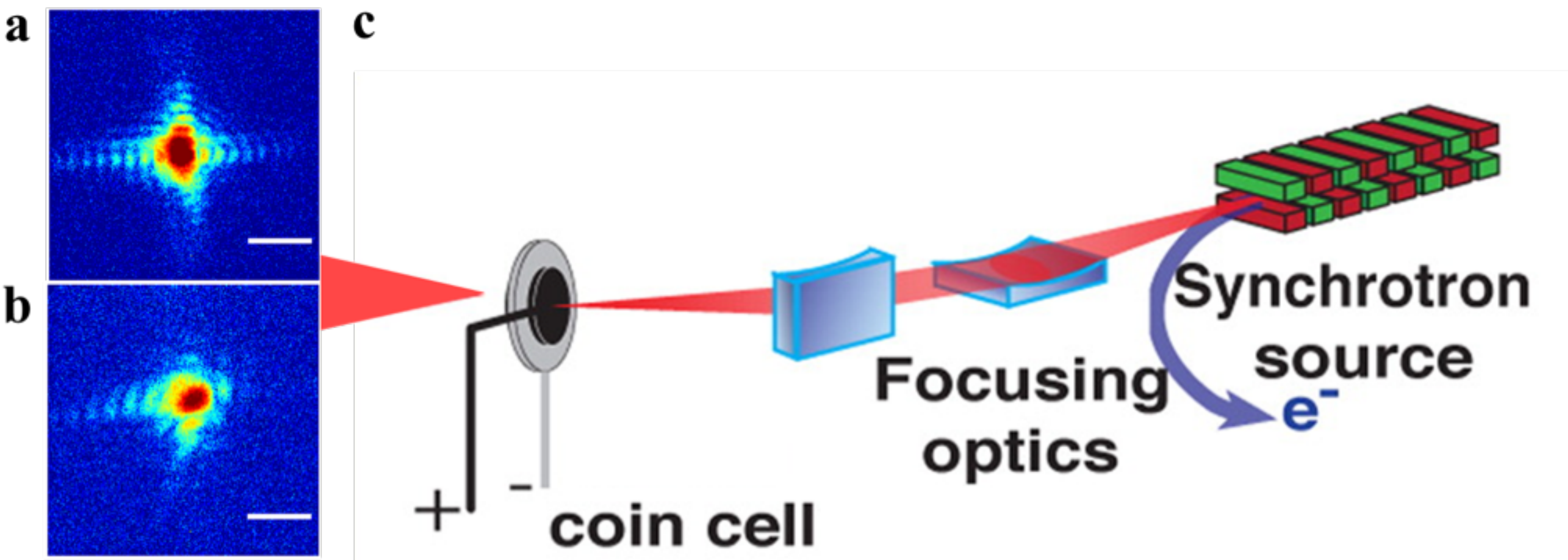
- ❑ After LLTO coating, there is a uniform nanoscale layer (around 1 nm in thickness) found on the particle surface. Surprisingly, the coating layer on LRLO particles is still conformal even after 200 cycles.

- ❑ The coating layer effectively prevents oxygen vacancy generation as well as cation rearrangement during cycling.

H.D. Liu, M. Zhang, Y.S. Meng et al., 2018, under review

Accomplishment to Date FY 18

BCDI Characterization on Single Particle of LRLO



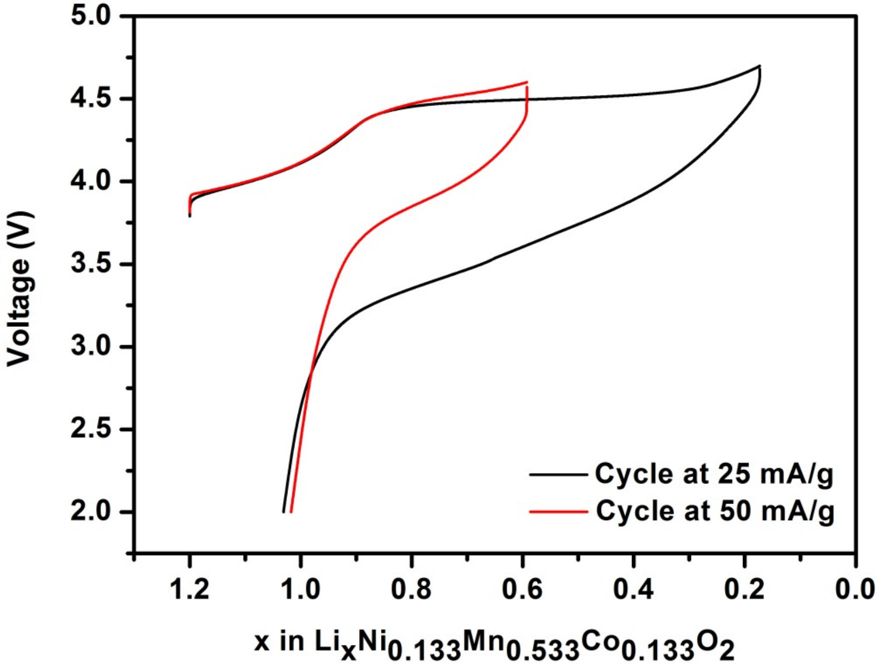
- Through the above setup, we demonstrated three-dimensional dislocation network formation by BCDI in LRLO during the initial charging process under operando conditions.

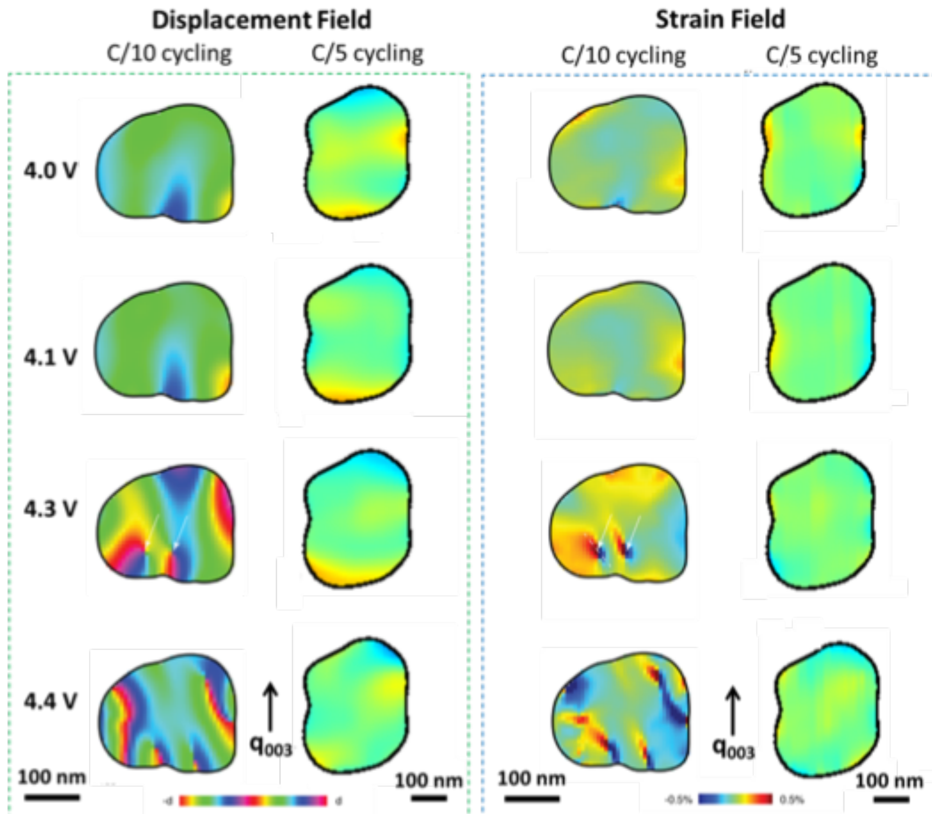
- The truncation rod in the diffraction speckle pattern is less symmetric for the sample after 50 cycles (b) compared with that of the sample after only 1 cycle (a), which typically indicates strain builds up in LRLO material during electrochemical cycling.

A. Singer, M. Zhang, Y.S. Meng et al., 2018, under review

Accomplishment to Date FY 18

BCDI Characterization on Kinetics in Single Particle of LRLO





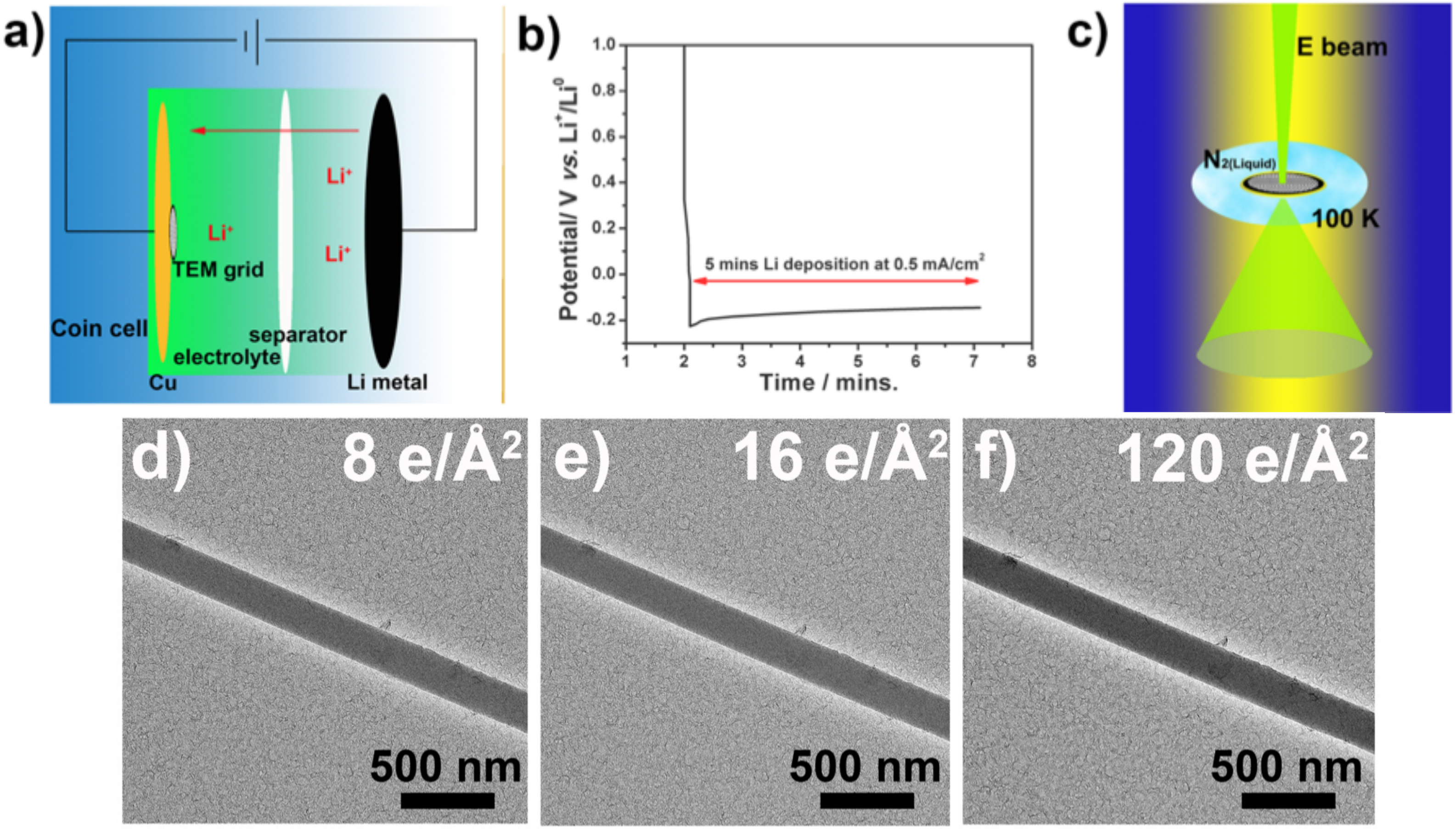
- ❑ Operando BCDI was carried on single particle when the battery was charged at different rates. No obvious difference was found in the voltage curve until ~4.35 V.

- ❑ At higher rate charging, less oxygen redox is activated due to sluggish kinetics so that less dislocation and strain network is formed in the bulk of LRLO particles.

A. Singer, M. Zhang, Y.S. Meng et al., 2018, under review

Accomplishment to Date FY 18

Observation of Li Dendrite Growth by Cryo-TEM

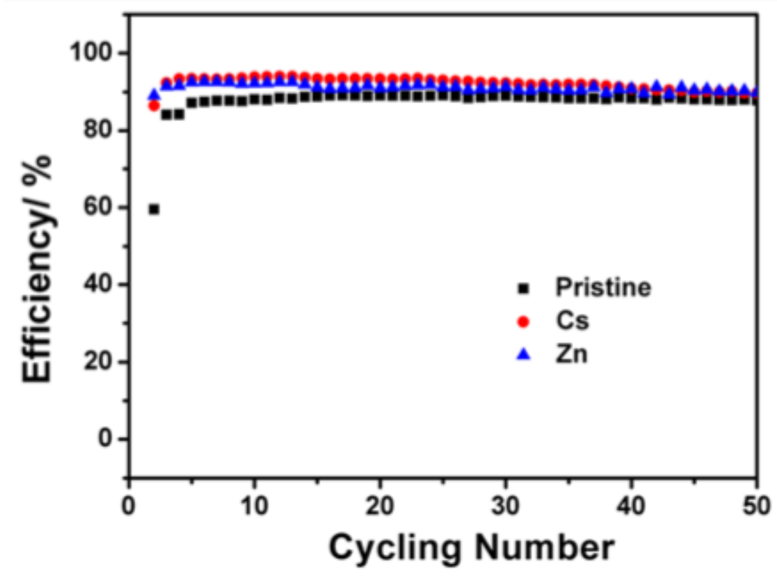


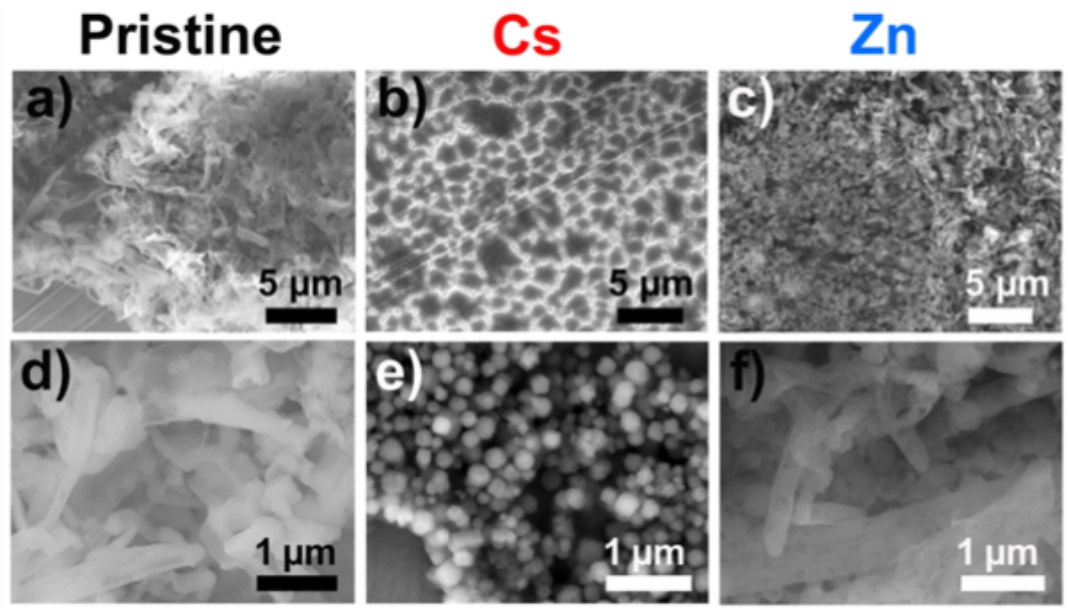
- ❑ Li metal is very stable at 100 K (d-f) and no visible changes are observed with the same magnification as the room temperature. Therefore, the cryo-TEM allows us to detect the Li metal at the nano scale while avoiding beam damage of the sample.

X. Wang, M. Zhang, Y.S. Meng et al., Nano Letters, 2017, 17 (12), 7606

Accomplishment to Date FY 18

Influence of Electrolyte Additive on Deposited Li Metal





- ❑ the CE of the cells improved when 50 mmol L^{-1} Cs^{+} and Zn^{2+} were added to the above carbonate electrolyte, which is 86% and 89% respectively at the 1st cycle.
- ❑ Clearly, dense interweaved Li films tend to form in the electrolytes with additives. In particular, Cs+ facilitates the Li metal to grow vertically and form aligned arrays.

X. Wang, M. Zhang, Y.S. Meng et al., Nano Letters, 2017, 17 (12), 7606

Responses to Previous Year Reviewers' Comments

No reviewer comments are available from previous year review on this project.

Collaboration and Coordination with Other Institutions

Dr. Ke An (ND)
Dr. Miaofang Chi (STEM/EELS)

Dr. Andrej Singer
(Operando BCDI)

Dr. Ross Harder
(Operando BCDI)

Dr. Bao Qiu and Dr. Zhaoping Liu
(Heat treatment of LRLO)

Remaining Challenges and Future Research

- The influence of lithium and oxygen migration during heat treatment on cation ordering in the TM layer will be studied in detail based on nudged elastic band (NEB) method from Ab initio computation.
- Control the anion activities (anion redox and oxygen evolution) in LRLO materials to optimize and stabilize the voltage operation, structure, and chemical interface.
- Other methods including pressure treatment is under investigation to recover the structure and voltage of LRLO material.
- Chemical composition and structure of electrochemically deposited Li metal at the nano scale will be further investigated for different electrolyte system using cryo-TEM.

Any proposed future work is subject to change based on funding levels

Summary

- A path to recover the layer structure and working voltage is designed through high-temperature annealing.

- The treatment at high temperature recovers the local Li-excess environments around oxygen, oxygen stacking sequence, and eliminates microstrain associated with different defects.

- BCDI measurements on LRLO single particle demonstrate significantly higher amount of defects generated when the material is charged at a lower rate.

- Cryogenic (cryo)-electron microscopy is a powerful tool to reveal the detailed structure of EDLi and the SEI composition at the nanoscale while minimizing beam damage during imaging.